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A CONTRIBUTION TO THE THERMAL CHEMISTRY OF PYRIDINE

by

VAN LORENS BOHNSON

A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF WISCONSIN
1916

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During the past few years considerable work has been done in this laboratory on the solubility of various inorganic salts in pyridine[1], a number of new compounds having pyridine of crystallization have been discovered, and the equilibria relations of these, together with those of many of the earlier known compounds, have been determined. It was frequently noted that the thermal effect accompanying the formation or the solution of these compounds was very appreciable.

The purpose of the work described in this paper, which is a continuation of the work of Krause[3] and Rottmann[10], was to measure the heat effects accompanying the act of taking on of pyridine of crystallization. Because of its analogy to the thermal effect accompanying the taking on of water of crystallization, which we call "heat of hydration", we shall, for lack of a better term, refer to the thermal effect under consideration as the "heat of pyridination".

This heat of pyridination was measured in the usual manner, i. e., by determining the heat of solution of the salt first without, and then with, its pyridine of crystallization, the difference between these values yielding the heat of pyridination.

Mathews and Germann[2], and others, have demonstrated the practicability of the Dewar flask as a protection against radiation in calorimetric measurements, and have shown that by its use a considerable degree of accuracy can be obtained. Although not capable of yielding the extreme accuracy attain-

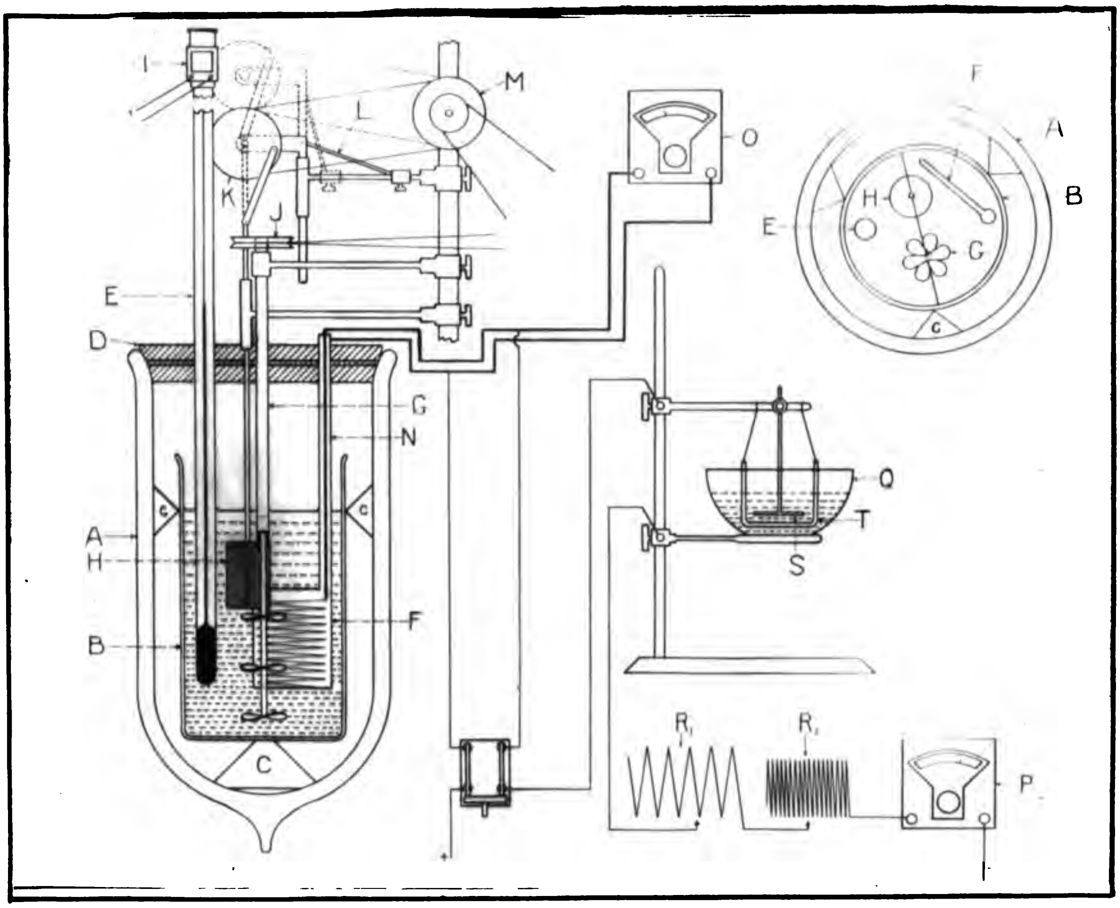
able with the adiabatic calorimeter, this form of calorimeter mantle offers greater ease in the making of thermal measurements than does the adiabatic. It has been in use in this laboratory for a number of years, and has proven to be very efficient; others also have used it with gratifying results, a fact which has frequently been recorded in the literature. Because of the rapidity with which operations can be carried out, this device was especially suited to the measurement of the heats of solution of compounds having pyridine of crystallization. The time factor was important, as some of these compounds have a considerable vapor pressure at room temperatures and lose pyridine readily, although for the most part they are fairly stable.

APPARATUS USED:

The heats of solution and the specific heats of the resulting solutions were determined by means of the same apparatus, which is illustrated in the diagram on page 3. This apparatus is a modification of that devised by Krause[3], and is, with but few changes, the one used by Rottmann[10].

A large Dewar flask (A) was used as the outer jacket. Inside of this flask, separated from it by an air space of about 1 cm., was the calorimeter proper (B), which was insulated from the Dewar flask by cork points (C) at the bottom and near the top.

The calorimeter (B), of about 600 cc. capacity, 8 cm. in diameter and 12 cm. high, was made of copper, nickel plated and


I
M
L
O
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c
R₁
R₂
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highly polished on the outside, and heavily plated with silver on the inside surface, silver being used because it resists the action of those solutions worked with, while copper is readily attacked.

The apparatus was stoppered with a flat cork (D) which had been cut into two cylindrical halves, and then glued together again with a sheet of ebonite 2 mm. thick between the halves. The ebonite served as an insulator and prevented the warping generally experienced with large corks. A double layer of tin-foil to prevent loss of heat through the stopper, was glued to its lower and lateral surfaces, and the stopper was then cut into two semicircular halves. It was perforated as shown, to accomodate the Beckmann thermometer (E) and the heating element (F) in opposite halves of the stopper. Along the cut diameter two small holes were made, one for the stirrer (G) and the other for the rod holding the platinum basket (H).

The Beckmann thermometer (E) was held in position by means of a cork stopper fitting the hole, so that the thermometer bulb was always immersed to the same depth. The heating element (F) was suspended in like manner. The thermometer was carefully standardized before using, by comparison with a laboratory standard thermometer, corrections for which were furnished by the United States Bureau of Standards. Both thermometers could be read to 0.001°. The comparison was made in an insulated calorimeter contained in a Dewar flask, the water being well stirred. The thermometers were tapped with a small buz-

zer (I) for ten seconds before each temperature was read; a small reading telescope supported on the thermometer facilitated the reading. In using the Beckmann thermometer, no correction for exposed thread was necessary, since it was used under the same conditions at which it was standardized. The probable error for the temperature reading being made in the course of this work was therefore not more than *0.001° to 0.002°.

The stirrer (G) consisted of a silver rod mounted with three propeller shaped double blades of silver 2 cm. long on either side of the rod. The end of the rod was cemented into a glass tube which led to a pulley (J). The speed of stirring was regulated by a resistance in the motor circuit. During the experiments described the rate was about 275 revolutions per minute. Neither the stirring nor the motion of the basket (to be described) had any appreciable thermal effect, the combined motions causing a rise in temperature of only about 0.001° in ten minutes.

The cylindrical basket (H), 2 cm. in diameter and 6 cm. long, made of fine platinum gauze, was fastened by platinum wire to a silver rod. The rod passed in turn through the opening between the halves of the stopper, through a sleeve to the pitman leading to the eccentric (K), which imparted an up and down thrust to the basket as the pulley revolved. The pulley (K) could be raised or lowered at will by means of the arm (L) and clamped in any desired position by a set-screw. When raised, the basket was supported above the liquid in the calor-

imeter; when lowered, it would be entirely submerged and would be thrust up and down in the liquid. The double pulley (M) allowed the basket to be plunged up and down, or to be held stationary, by merely shifting the belt from the fixed to the free pulley. During the process of solution the basket plunged up and down in the solvent at a rate of about 125 times per minute.

The heating element (F) was constructed as follows;[3,10] A suitable length of No. 36 nichrome wire to give a resistance of about 40 ohms was wound at small intervals about a thin mica sheet, 3.5 cm. X 4.5 cm. in size. Two other sheets, a trifle larger, were placed on either side, and the resistance unit so prepared was slipped into a thin brass case made for the purpose by flattening a large brass tube. One end of the wire was soldered to the lower edge of the casing and the other to the end of a well-insulated heavy copper wire, which was contained in a small brass tube (N). The tube was firmly fastened to one of the upper corners of the case, and all joints were pressed together, soldered, and filed smooth. The heating element was then cleaned, plated with a thin coating of copper, then with silver. The completed heating blade was 4 cm. wide, 5 cm. long, and about 2 mm. thick. The brass tube (N) was 13 cm. long, and 2.5 mm. in diameter. Since the resistance of the heavy copper wire in the circuit was negligible in comparison with the resistance of the nichrome wire, the heating effect took place only in the blade of the heater. With a

potential drop of about 30 volts across this resistance, the solution could be heated sufficiently in two to three minutes (giving a rise in temperature of from 3° to 4°) to determine its specific heat.

Across the terminals of this heating element were connected, by means of a very heavy insulated copper wire, the terminals of a Weston Direct Reading Laboratory Standard Voltmeter (O), having a 30 cm. scale graduated to hundredths and capable of estimation to thousandths of a volt. A correction curve for the instrument was obtained by comparing it with a voltmeter of the same type which had been standardized by the Bureau of Standards. At the voltage used in these experiments, the correction to be applied to the scale reading was +0.010 volt. Storage batteries were used as a source of current, and the voltage was kept at precisely the desired point by means of the sliding resistances (R_1 and R_2) in the circuit.

An ammeter (P) was connected in series, and was used only to get an approximate value of the current.

The current passing through the heater was measured accurately by means of a silver coulometer (Q). The anode (S), consisting of a sheet of platinum foil heavily plated with electrolytic silver, fastened to a heavy platinum wire, was contained in a porous cup (T), (as recommended by Richards), 6 cm. in diameter and 7 cm. high, which was suspended from the arm of the electrolyzing stand by platinum wires. The cathode was a platinum dish about 13 cm. in diameter at the

top and 4 cm. deep. A neutral 15% solution of silver nitrate was used as electrolyte.

MATERIALS USED:

The silver nitrate used in the coulometer was Merck's "tested purity" which was recrystallized from doubly distilled water. A 15% solution was made and allowed to stand over metallic silver. When used, the solution was neutral to litmus.

The pyridine used as a solvent and in the preparation of the various compounds was Merck's "medicinal", which was purified according to the method of Wilcox[4]. It was first allowed to stand over electrolytic stick potassium hydroxide for several months, was digested with potassium permanganate and barium oxide for eight hours under a reflux condenser, and the fraction distilling over between 114.6° and 115.6° at 737 mm. was preserved for use. It was found that after the pyridine had been redistilled several times, the greater portion distilled over at 115.4° at 737 mm.

The Merck's C. P. mercuric chloride and mercuric iodide used were found on analysis to be of a high degree of purity, and required no further purification.

The water used in the preparation of solutions and in washing the silver deposit in the coulometer was specially distilled for the purpose.

PREPARATION AND ANALYSIS OF COMPOUNDS:

It has been shown by McBride[5] that the salts $3HgCl_2 \cdot 2C_5H_5N$, $HgCl_2 \cdot C_5H_5N$, and $HgCl_2 \cdot 2C_5H_5N$ exist, and separate out in crystalline form at definite temperatures. These compounds have also been previously described by Monari[6], by Lang[7], and by Pesci[8].

The compound $HgI_2 \cdot 2C_5H_5N$ was also first described by Monari[6], and later by other investigators. The solubility of mercuric iodide in pyridine has recently been determined by Ritter[9], who has shown that between the limits -50° and +100°C., $HgI_2 \cdot 2C_5H_5N$ is the only compound of mercuric iodide and pyridine, though it occurs in two different crystalline forms.

The compound $HgCl_2 \cdot 2C_5H_5N$ separates from a pyridine solution of mercuric chloride below 76°. A solution saturated at 65° was cooled and the salt allowed to crystallize. The crystals after being pressed were dried by placing them in a glass tube through which dry air was being drawn at room temperature. Analyses yielded the following results:

Weight of sample	Weight of HgS	Percentage of Hg	Theoretical % Hg
1.1612 g.	1.6870 g.	46.69	46.69
.6289 g.	.9123 g.	46.63	

The compound separated in large needle-shaped crystals. It tends to lose pyridine in the air, and was therefore kept in tightly stoppered bottles.

An attempt was made to prepare the compounds $3HgCl_2 \cdot 2C_5H_5N$,

and $HgCl_2 \cdot C_5H_5N$, which separate out at 117° and at 80° , respectively, by allowing them to crystallize from pyridine solution at these temperatures, but the difficulty of freeing the crystals of all adhering pyridine at the temperatures of formation, and the fact that unless the pyridine is so removed the compounds will revert in whole or in part to $HgCl_2 \cdot 2C_5H_5N$, caused the method to be abandoned. Recourse was then had to the methods described below.

The compound $3HgCl_2 \cdot 2C_5H_5N$ was prepared as described by Pesci[8], by adding solid $HgCl_2 \cdot 2C_5H_5N$ to a boiling 4% aqueous solution of mercuric chloride, until no more would dissolve, filtering, and allowing to cool. The product separated in white needle shaped crystals, which were dried in the air over night. Analyses of three separately prepared samples yielded the following results:

	Weight of sample	Weight of HgS	Percentage of Hg	Theoretical % Hg
1.	0.7442 g.	0.5336 g.	61.82	61.87
	0.9477 g.	0.6804 g.	61.90	
2.	0.8426 g.	0.6066 g.	62.07	
	0.8654 g.	0.6234 g.	62.11	
3.	0.6944 g.	0.4991 g.	61.97	
	0.9570 g.	0.6898 g.	62.14	

These three samples were kept separate in tightly stoppered bottles, and the heat of solution was separately determined for each sample. The substance was stable in the air, but

in the presence of pyridine vapor tended to form the compound $HgCl_2 \cdot 2C_5H_5N$.

The compound $HgCl_2 \cdot C_5H_5N$ was prepared as described by Lang[7]. An aqueous solution of mercuric chloride was treated with an excess of pyridine. The voluminous white precipitate thus formed was boiled up with distilled alcohol, the solution filtered through a hot water funnel, and allowed to cool. The product separated in long, white, hair-like crystals, tending to form radiating aggregates. The crystals were filtered, pressed, and allowed to dry over night in the air, as at ordinary temperatures the salt is quite stable. Analyses yielded the following results:

Weight of sample	Weight of HgS	Percentage of Hg	Theoretical % Hg
0.8130 g.	0.5402 g.	57.29	57.23
.7400 g.	.4920 g.	57.32	

The compound $HgI_2 \cdot 2C_5H_5N$ separates out from pyridine solution at ordinary temperatures, and was thus prepared. The needle-like crystals were filtered, pressed, and dried in a long glass tube by passing over them a current of dry air. Analyses yielded the following results:

Weight of sample	Weight of HgS	Percentage of Hg	Theoretical % Hg
0.9408 g.	0.3540 g.	32.45	
1.0332 g.	0.3910 g.	32.54	32.75
0.9502 g.	0.3591 g.	32.58	

In weighing out the necessary amount of salt for use in determining its heat of solution, allowance was made for the fact shown in the analysis that all excess pyridine had not been removed. The salt is unstable in the air, decomposition making itself evident by a color change from white to red through intermediate stages.

Methods of Analysis:

In the case of mercuric chloride and its compounds with pyridine, the method of analysis described by McBride[5] was used. A sample of about half a gram was dissolved in dilute hydrochloric acid, and the whole diluted to about 100 cc. Hydrogen sulphide was then passed through the solution in the cold, until the mercuric sulphide was completely precipitated. The precipitate was filtered through a tared Gooch crucible, washed several times with hot distilled water, with alcohol, and with carbon bisulphide, dried for two hours at 110° in an oven, and weighed.

In the case of mercuric iodide and its compounds with pyridine, the method of analysis described by Ritter[9] was used. A sample of about half a gram was dissolved in an excess of potassium iodide solution, and the whole diluted to about 250 cc. Hydrogen sulphide was passed through the solution in the cold until the mercuric sulphide was completely precipitated. This was allowed to stand about an hour, was then filtered, washed, and dried, as described above, and weighed.

PROCEDURE:

An exact amount of purified pyridine (400 g., as this filled the calorimeter to the best working capacity) was weighed out in the calorimeter, and the vessel and its contents were allowed to come to a temperature slightly above or below room temperature, depending upon whether the thermal change would produce a rise or a fall in temperature, after which the calorimeter was placed in the Dewar flask. The salt to be used was weighed out in the platinum basket, in the ratio of 1 mole of salt to 200 moles of solvent. The stirrer was then adjusted, and the basket attached to the eccentric in such a position that it was supported above the liquid. The two halves of the stopper, carrying the thermometer and the heating element, were pressed into place, and the motor started. Since the belt was on the free pulley, the basket remained stationary above the pyridine. The stirring was allowed to continue for ten minutes or more, until it was evident that the change in temperature was regular. Temperature readings were taken every minute, and from this time-temperature curve, the radiation in the fore-period was obtained.

When the temperature change had become regular, the belt was shifted from the free to the fixed pulley and the arm (L) was adjusted so as to lower the basket into the solvent. At this instant the time and temperature were noted. The basket plunged up and down, effecting complete solution in a short time, the maximum change in temperature taking place in all cases in about two minutes. The highest (or lowest) tempera-

ture was recorded, with the time, and readings were thereafter made each minute for about twenty minutes in order to obtain the radiation for the after period.

The specific heats of the solutions were sometimes obtained immediately after the above procedure, without removing the solution from the apparatus. In most cases, however, the solution was removed, cooled to the desired temperature (about two degrees below room temperature), and a weighed amount of solution (400 g.) replaced in the calorimeter. The apparatus was then set up as before, and the stirring allowed to continue until the temperature change had become uniform. The coulometer having been made ready, the switch was closed, and a definite current was passed through the heater for a length of time necessary to produce a rise in temperature of about 4° C. In all the results reported, the voltage was kept precisely at 30.1 by means of the sliding resistances. After cutting off the current, readings of temperature were made each minute, as before, for about twenty minutes. Immediately after the current was cut off, the electrolyte was poured out of the coulometer, to avoid re-solution of the silver. The silver deposit in the platinum dish was carefully washed with distilled water and alcohol, and dried in an air bath at 110° for two hours, allowed to cool, and weighed.

The water equivalent of the apparatus was obtained experimentally by passing a definite current through the heating element, thus adding a known amount of heat when the calorimeter

contained a known weight of water. The difference in the amount of heat accounted for by the change in temperature of the water and that produced by the current must have been taken up by the apparatus. Dividing this amount by the corrected rise in temperature gave the water equivalent of the apparatus, which was found to be 34.626 grams. Slight changes made in the apparatus later caused a change in the water equivalent in most of the experiments to 34.911 grams.

Determination of Water Equivalent

Weight of silver	Volts	Temperature change	Weight of water	Water Equivalent
0.2156 g.	30.1	3.194°	400 g.	34.634
.2644	"	3.917°	"	34.622
.2838	"	4.210°	"	34.044
.2249	"	3.123°	"	35.186
.2360	"	3.498°	"	34.407
.2324	"	3.441°	"	34.867
			Mean	34.626

Correction: 5.10 g. of silver plating was added to the calorimeter. 5.1 x .0559 (sp. ht. of Ag) = .285

34.626

34.911

CALCULATIONS:

Table of Symbols Used

H = water equivalent of apparatus

Q = quantity of heat (in calories) produced by current

W = weight of liquid (in grams)

T = corrected rise (or lowering) of temperature

C = amperes

t = time of flow of current (in minutes)

R = resistance

A = weight of silver (in grams)

E = volts

S = specific heat

M = molecular weight of salt

X = weight of salt used (in grams)

dT = average rate of change of temperature in fore-period

dT' = " " " " " " " after-period

n = number of minutes in middle-period

Formulas Used in Calculations

(1) The water equivalent of the apparatus was calculated by means of the formula:

$$H = \frac{Q - (W \times S \times T)}{T}$$

Since $Q = C^2Rt$, $\frac{E}{C} = R$, and $C = \frac{96580 \times A}{107.9 \times t}$, the following expression may be obtained:

$$Q = \frac{96580 \times A \times E}{107.9 \times 4.177}$$

(4.177 j = 1 calorie
= 4.177 volt-coulombs
at 21° C)

or, $Q = K \times A \times E$, where the constant $K = \dfrac{96580}{107.9 \times 4.177}$

$$= 214.29$$

Hence, since the specific heat of water at 21° is 1.00191, the first equation given above becomes:

$$H = \frac{K \times A \times E}{T} - (W \times 1.00191)$$

(2) The specific heats of the solutions used were obtained by substitution in the equation:

$$S = \frac{\frac{Q}{T} - H}{W}$$

which resolves itself into:

$$S = \frac{\frac{K \times A \times E}{T} - H}{W}$$

(3) The heats of solution were obtained by substitution in:

$$\text{Heat of Solution} = T\frac{M}{X}\left[(W \times S) + H\right]$$

(4) The corrected rise in temperature T was obtained by adding to the observed rise the correction for the thermometer, C_1 , obtained from the correction curve, and the radiation correction, C_2 , which was calculated by means of the expression:

$$C_2 = \frac{n}{2}(dT + dT')$$

All experimental work was conducted with an endeavor to make

the radiation of heat to the calorimeter in the fore-period as nearly equal as possible to the radiation from the calorimeter in the after-period, thus minimizing this correction. The values for dT and dT' were taken to be - when the temperature was rising, and + when it was falling, and the correction C_2 was added to the observed change in temperature.

The correction for additional heating effect due to the motion of basket and stirrer was determined, found to be about + 0.001° in ten minutes, and was therefore negligible in view of the short time necessary to obtain the total change in temperature.

RESULTS:

The specific heat of pure pyridine, the heats of solution of mercuric chloride and mercuric iodide and their various "pyridinates", with the specific heats of the resulting solutions, are given below in tabular form. In each case 400 grams of pyridine were used, with such amounts of salt as would make the ratio of salt to pyridine 1 mole of the former to 200 moles of the latter, due allowance being made, of course, for the pyridine of crystallization.

It should be noted that the mean value of the specific heats obtained in the various determinations was used in the calculation of the heats of solution. It will also be noted that the specific heats of the different solutions of mercuric chloride and its pyridinates are approximately the same, or that the difference in their values does not exceed

the possible experimental error. This of course should be the case since these solutions vary from one another in composition only by a very small weight of pyridine. The same consideration holds with the solutions of mercuric iodide and its pyridinates.

TABLE I.

Specific Heat of Pyridine (at 21°)

Weight of silver	Volts	Temperature change	Weight of pyridine	Specific Heat
0.0992 g.	30.1	+ 3.344°	400 g.	0.3918
.0901	"	3.027°	"	.3934
.1172	"	3.950°	"	.3919
.1144	"	3.853°	"	.3922
.1245	"	4.190°	"	.3925
			Mean	0.3923

Water equivalent = H = 34.626

TABLE II.

$HgCl_2$ in Pyridine.

Weight of salt	Weight of pyridine	Temperature change	Heat of Solution
6.8696 g.	400 g.	+ 1.743°	+ 13,405 cals
"	"	1.743°	13,405
"	"	1.740°	13,382
"	"	1.745°	13,421
"	"	1.744°	13,413
	Mean	1.743°	+ 13,405 cals

Weight of silver	Volts	Temperature change	Weight of solution	Specific Heat
0.0890 g.	30.1	+ 2.950°	406.8696 g.	0.3924
.1364	"	4.584°	400.000	0.3925
.0978	"	3.240°	406.8696	0.3927
.0984	"	3.259°	406.8696	0.3924
			Mean	0.3925

H = 34.911

TABLE III.

$3HgCl_2\cdot 2C_5H_5N$ in pyridine

Sample[α]	Weight of salt	Weight of pyridine	Temperature change	Heat of Solution
(1)	8.2029 g.	400 g.	+ 0.648°	+ 4,985 cals
(2)	"	"	.647°	4,978
(3)	"	"	.650°	5,001
3 samples mixed		"	.647°	4,978
		Mean	+ 0.648°	+ 4,985 cals

Weight of silver	Volts	Temperature change	Weight of solution	Specific Heat
0.1188 g.	30.1	+ 3.994°	400 g.	0.3924
.1177	"	3.991°	"	.3883
.1294	"	4.362°	"	.3911
.1265	"	4.251°	"	.3926
			Mean	0.3913

H = 34.911

α - see page 10.

TABLE IV.

$HgCl_2 \cdot C_5H_5N$ in Pyridine

Weight of salt	Weight of pyridine	Temperature change	Heat of Solution
8.8695 g.	400 g.	+ 0.248°	+ 1,912 cals
"	"	.252°	1,943
"	"	.253°	1,951
	Mean	+ 0.251°	+ 1,935 cals

Weight of silver	Volts	Temperature change	Weight of solution	Specific Heat
0.1208 g.	30.1	+ 4.062°	400 g.	0.3922
.0904	"	3.029°	"	.3940
.1162	"	3.920°	"	.3908
.1088	"	3.674°	"	.3902
			Mean	0.3918

H = 34.911

TABLE VI.

HgI_2 in Pyridine

Weight of salt	Weight of pyridine	Temperature change	Heat of Solution
11.4973 g.	400 g.	+ 1.317°	+ 9,961 cals
"	"	1.322°	9,999
"	"	1.323°	10,000
	Mean	+ 1.321°	+ 9,987 cals

Weight of silver	Volts	Temperature change	Weight of solution	Specific Heat
0.1276 g.	30.1	+ 4.402°	400 g.	0.3801
.1296	"	4.466°	"	.3806
.1222	"	4.217°	"	.3800
			Mean	0.3802

H = 34.911

TABLE VII.

$HgI_2 \cdot 2C_5H_5N$ in Pyridine

Weight of salt	Weight of pyridine	Temperature change	Heat of Solution
13.4973 g.	400 g.	- 0.647°	- 4,922 cals
"	"	.647°	4,922
"	"	.650°	4,944
	Mean	- 0.648°	- 4,929 cals

Weight of silver	Volts	Temperature change	Weight of solution	Specific Heat
0.1286 g.	30.1	+ 4.413°	400 g.	0.3826
.1216	"	4.201°	"	.3795
.1042	"	3.592°	"	.3805
.1236	"	4.256°	"	.3812
			Mean	0.3809

H = 34.911

From the foregoing results, the thermal changes taking place in the formation of the various pyridinates may be calculated, as follows: ("Py" represents a quantity of pyridine indicated by the ratio 1 mole of salt to 200 moles of pyridine)

$HgCl_2 + Py = HgCl_2 \cdot Py + 13,405$ cals (1)
$3HgCl_2 \cdot 2C_5H_5N + Py = 3HgCl_2 \cdot Py + 14,955$ cals (2a)
(or $HgCl_2 \cdot 2/3C_5H_5N + Py = HgCl_2 \cdot Py + 4,985$ cals) (2b)
$3HgCl_2 + 2C_5H_5N = 3HgCl_2 \cdot 2C_5H_5N + 25,260$ cals (3a)
(or $HgCl_2 + 2/3C_5H_5N = HgCl_2 \cdot 2/3C_5H_5N + 8,420$ c) (3b)

$HgCl_2 + Py = HgCl_2 \cdot Py + 13,405$ cals (1)
$HgCl_2 \cdot C_5H_5N + Py = HgCl_2 \cdot Py + 1,935$ cals (4)
$HgCl_2 + C_5H_5N = HgCl_2 \cdot C_5H_5N + 11,470$ cals (5)

$HgCl_2 + Py = HgCl_2 \cdot Py + 13,405$ cals (1)
$HgCl_2 \cdot 2C_5H_5N + Py = HgCl_2 \cdot Py - 5,372$ cals (6)
$HgCl_2 + 2C_5H_5N = HgCl_2 \cdot 2C_5H_5N + 18,777$ cals (7)

$HgCl_2 + 2C_5H_5N = HgCl_2 \cdot 2C_5H_5N + 18,777$ cals (7)
$HgCl_2 + C_5H_5N = HgCl_2 \cdot C_5H_5N + 11,470$ cals (5)
$HgCl_2 \cdot C_5H_5N + C_5H_5N = HgCl_2 \cdot 2C_5H_5N + 7,307$ cals (8)

$HgI_2 + Py = HgI_2 \cdot Py + 9,987$ cals (9)
$HgI_2 \cdot 2C_5H_5N + Py = HgI_2 \cdot Py - 4,929$ cals (10)
$HgI_2 + 2C_5H_5N = HgI_2 \cdot 2C_5H_5N + 14,916$ cals (11)

SUMMARY:

(1) It is evident that the thermal effect accompanying the combination of metallic salts with organic compounds of crystallization may in many cases be of considerable magnitude; in fact, the values are comparable with the analogous heats of hydration of such substances as sodium sulphate, etc.

(2) A satisfactory apparatus for the measurement of heats of solution and specific heats of solutions has been devised and described. It has been applied to the measurement of the heats of solution in pyridine of mercuric chloride and mercuric iodide and their compounds with pyridine.

(3)

(a) The heat of formation of one mole of $3HgCl_2 \cdot 2C_5H_5N$ from $3HgCl_2$ and $2C_5H_5N$ at 21° is + 25,260 calories or 105,511 joules[α]. (From $HgCl_2$ and 2/3 C_5H_5N it is + 8,420 calories or 35,170 joules.)

(b) The heat of formation of one mole of $HgCl_2 \cdot C_5H_5N$ from $HgCl_2$ and C_5H_5N at 21° is 11,470 calories or 47,910 joules.

(c) The heat of formation of one mole of $HgCl_2 \cdot 2C_5H_5N$ from $HgCl_2$ and $2C_5H_5N$ is 18,777 calories or 78,431 joules; from $HgCl_2 \cdot C_5H_5N$ and C_5H_5N is 7,307 calories or 30,521 joules.

(d) The heat of formation of one mole of $HgI_2 \cdot 2C_5H_5N$ from HgI_2 and $2C_5H_5N$ is 14,916 calories or 62,304 joules.

[α] 1 calorie (21°) = 4.177 joules.

The writer wishes to express his appreciation to Dr. Mathews for the suggestion at which this research was undertaken, and for the constant helpful assistance which he has rendered during its progress.

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May, 1916.

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Approved by JH Mathews

May 31, 1916

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